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Barium Grease

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Introduction

During the past fifteen years the grease industry has witnessed a number of valuable and progressive developments which clearly reveal a vitality within the industry itself as well as suggest an interesting and very promising future. These developments have related both to the improved formulation of the more conventional greases, such as those thickened with aluminum, calcium and sodium soaps, and to more significant testing methods for evaluating these same lubricants. During the same period, the introduction of several entirely new types of greases has also represented a contribution of considerable interest and importance. Of these new types, the barium and lithium soap-thickened lubricants are probably the most widely known and used. This paper is concerned specifically with the barium soap greases and the purpose of the subsequent discussion is to present in adequate detail the methods of compounding these greases, their properties, uses and future possibilities.

It will be recalled that until recent years the three principal types of greases marketed by the trade were those prepared with the calcium, sodium or aluminum soaps as oil thickeners. Except in a limited degree, none of these greases combine all the principal desirable properties of an all-purpose grease. The lubricants thickened with sodium soap exhibit little resistance to the emulsifying action of water but in general, provided water is not present, do furnish acceptable lubrication at elevated temperatures. The common calcium soap greases are relatively resistant to the action of water, but normally cannot be used safely at elevated temperatures either because they are too fluid at temperatures above approximately 150°F. or because at temperatures approaching 200°F. the loss of water of hydration results in separation of oil and soap. Through the judicious combination of other soaps with sodium soap, the use of viscous oils or special fats in the manufacture of sodium soap greases, or through the use of high boiling organic compounds, etc., in the case of calcium greases, the cited defects of the two classes of greases can be mitigated but not entirely eliminated. The aluminum base greases combine water and heat resistance to an interesting degree, but these greases unless appropriately modified often possess objectionable gel structures at elevated temperatures, precluding their satisfactory use at such temperatures.

A few years ago consideration was given to the possibility that barium might form soaps that would thicken mineral oil and yield all-purpose greases providing high-temperature lubrication as well as water resistance. The greases originally contemplated were those containing normal soaps such as are used in the case of calcium base greases. The few references in the literature indicated that normal barium soap greases of acceptable quality had never been prepared successfully. Nevertheless, it was considered worthwhile to re-investigate the problem, and initial attempts to produce these greases consisted in using a procedure similar to that currently employed for the ordinary lime soap greases.

The results of the above investigation were unexpected and extremely interesting. It was found that while relatively stable normal barium soap greases could be prepared, they required water for their stabilization and consequently did not possess sufficient advantages over calcium soap greases in respect to dropping point, temperature susceptibility and stability, to justify manufacture. However, during the investigation the discovery was made that under certain conditions excess barium hydroxide would react with normal barium soap to yield a soap complex which in turn would thicken mineral oils and yield the desired water and heat-resistant grease. Full information upon the subject was disclosed in two patents[1] covering the composition and compounding procedures of the aforementioned greases.

After an extended study of the service performance of the above "complex" barium greases and the development of suitable methods for commercial manufacture, it was found possible to market the grease as a regular product and to produce it with the same personnel and equipment as were used for the more conventional sodium and calcium soap greases. Since that time, for a period of over six years, the complex barium soap greases have been marketed regularly in increasing volume and, as will be discussed later in more detail, their performance in service has fulfilled expectations.

The following pages present a detailed discussion of manufacturing methods, properties, current uses, and future possibilities of complex barium soap greases.

The Preparation of Commercial Barium Soap Greases

The commercial preparation of complex barium soap greases is given in broad form with extensive detail in the two patents[1] cited above, but the following outline covers the salient features of one of the preferred methods:

The appropriate fat or fatty mixture, such as prime tallow, and the barium hydroxide (usually in the form of barium hydroxide octahydrate) in specified excess amounts are charged to a jacketed kettle equipped with

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Report on Grease Dropping Point Methods

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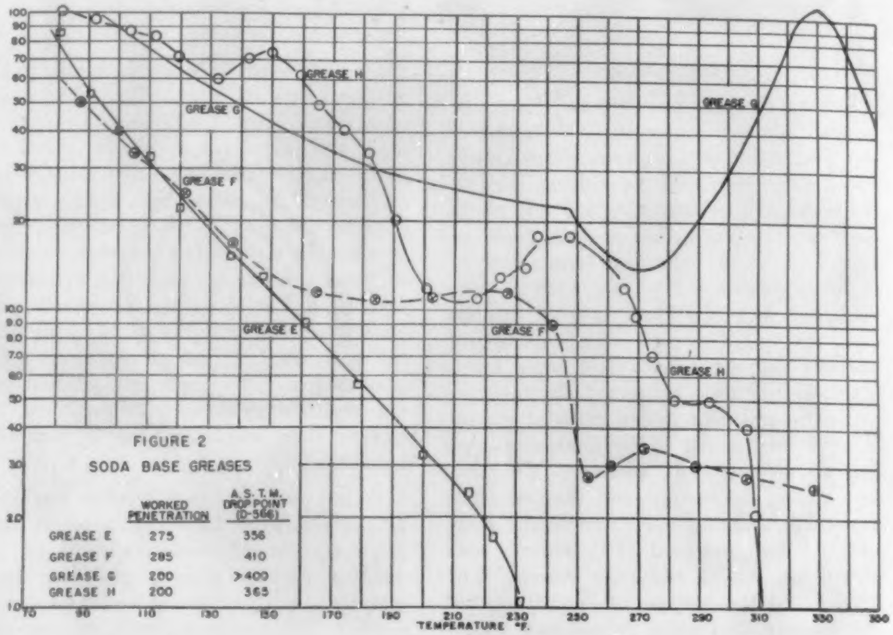
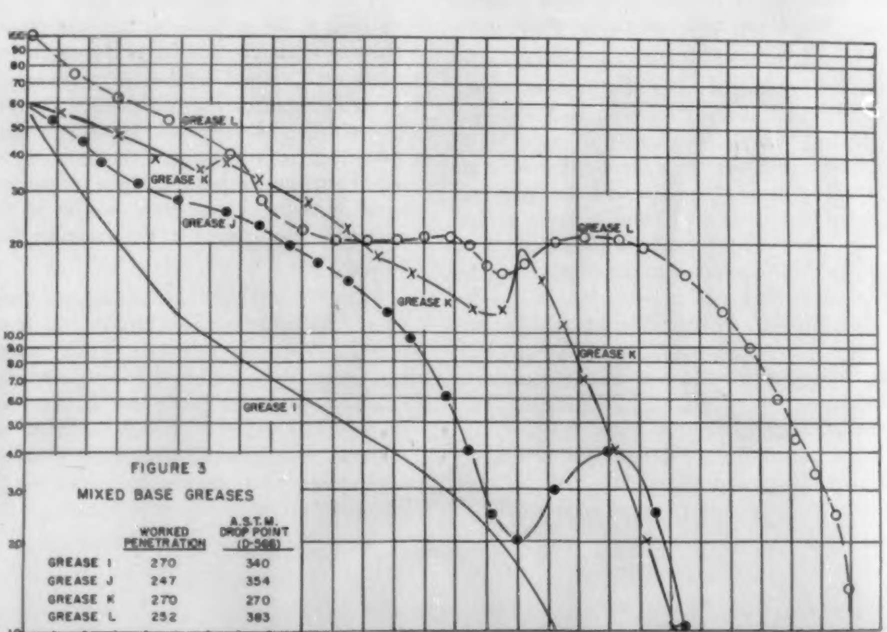
(Continued from March Issue)

Figure 2 shows similar data for four soda base greases. These products are of the short fiber or smooth structure types recommended and extensively used for anti-friction bearing lubrication. Grease E and F are of medium consistency, NLGI #2, while G and H conform to the #3 grade. Obviously the higher soap content (28 to 30%) of the latter two products is partly responsible for their higher viscosities at elevated temperatures, in comparison with E, containing 17.5% of soap. Grease F, however, contains 21% soap, yet compares reasonably well with Grease H, at least up to 250°F. The greases increase in dropping points in the following order: E, H, F, and G, and the temperatures at which their viscosities approach that giving rise to 1.0 lbs./in.² flow resistance under the test conditions are in the same sequence. However, in all cases the latter temperature is lower than the dropping point, with Grease E showing the largest difference of some 125°F. The arbitrarily set limit of 1.0 lb./in.² pressure was chosen since it is probable that a grease having this low resistance to flow would tend to leak out of a small clearance under very slight stress, such as the turbulence in a bearing might produce. Thus, it is unlikely that Grease E would be suitable at temperatures beyond 230°F, Grease H beyond 310°F, while Grease G may be satisfactory at temperatures up to 350°F. These latter two products are known to have been successfully employed in severe, high temperature, ball bearing service.

There is one other significant detail which this type of investigation reveals. The slope of the pressure temperature curve for Grease F changes very rapidly at about 240°F. This rapid loss of viscosity with temperature corresponds to a softening or loosening of the grease's soap structure and indicates a tendency to liberate oil. If appreciable oil separation should occur at this stage, a hard, dry residue of high soap content might be left in the bearing as a potential source of eventual lubrication failure. It would be of particular interest to obtain data on the performance of Grease G on prolonged use at 240 to 250°F.

The mixed or modified soda base greases have characteristics essentially similar to the straight soda type, which is to be expected since the major thickening constituent still is soda soap. The most significant fact, illustrated in Figure 3, is the wide discrepancy between drop point and minimum grease viscosities. Grease K has a drop point of 270°F, but at this temperature the viscosity has not dropped enough to give a flow resistance of 1.0 lb./in.². Moreover, at its drop point (270°F) this grease has the same apparent viscosity that Greases I and J have at some 120°F below their dropping points. At 230°F Grease K is about 15 times as viscous as Grease I, al-





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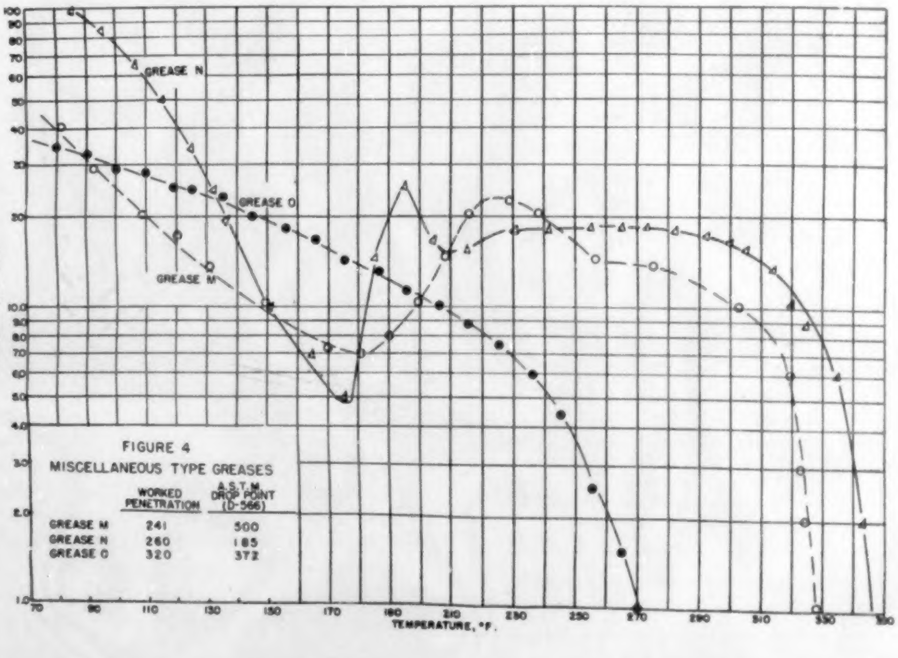
though the latter has a dropping point 70°F higher than K. These data illustrate quite strikingly the difficulties which may be encountered when attempting to predict high temperature performance from dropping point values.

Figure 4, which gives data on lithium, aluminum and barium soap greases, illustrates some interesting characteristics. The barium soap grease appears to have adequate high temperature resistance up to about 320°F where an abrupt drop in viscosity occurs. The lithium stearate grease O shows a gradual drop in resistance to flow up to some 230°F, beyond which the rate accelerates to give a 1.0 lb./in.^{2} at 270°F. Grease N, an aluminum stearate type shows a very rapid increase in viscosity at about 175°F. This corresponds to the transition from the gel to the elastic or rubbery state, which is experienced at this temperature range during manufacture of this type of grease. In this rubbery cohesive state the material is not very satisfactory as a lubricant, since it tends to ball up and pull away from the bearing surface. This observation stresses the fact that the viscosity-temperature test cannot be used as the sole criterion for suitability of all types of grease for high temperature service. The grease must be examined during the run at frequent intervals as a check on its condition, with respect to soap granulation, oil separation, or marked change in structure, such as we encountered with aluminum soap grease.

The only working to which the grease is subjected during the viscosity determination over a range of temperatures in the SOD Pressure Viscosimeter is that inherent in the deformation which occurs when the grease enters the capillary. On the other hand, in a bearing the portion of the lubricant on the moving surface is subjected to much more intensive working over prolonged periods. While this condition cannot be readily duplicated in a simple laboratory test apparatus not involving a bearing as the test element, the grease can be subjected to considerably more working in the viscosity-temperature test by passing it through the Zenith gear pump employed in the viscosimeter rather than merely extruding it from a cylinder through the capillary. In order to investigate the effect of increased working of the grease during the viscosity determination, the Esso Laboratories have modified a viscosimeter in which the grease will be passed through the pump into the capillary.

The data on the variation of viscosity with temperatures, which has been presented, indicates that this type of test offers promise as a means of estimating the performance of several types of greases at elevated temperatures. A great deal of additional work, particularly correlation of the viscosity-temperature data wtih service experience in high temperature applications, remains to be done. Also, while the viscosity-temperature data on greases may be expected to give valuable information on the behavior of greases at elevated temperature, factors not evaluated by this type of test will also have to be considered. Among these may be included the resistance to oxidation and subsequent change in consistency, the tendency of the oil to evaporate at elevated temperatures, in case of products containing low flash point oils, and obvious changes in structure, such as encountered with the aluminum base Grease N. Any of these factors may make a given grease unsuitable for high temperature service, regardless of excellent temperature-viscosity characteristics.



Barium Grease

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an agitator and supplied with 110-120 pound steam. While being agitated, the mass is heated to a temperature somewhat above the boiling point of water, e.g. 214°F., for a time sufficient to allow completion of the saponification process. After the fat has been saponified, which is a matter of a relatively few minutes, heating of the batch is continued and approximately half of the mineral oil is slowly incorporated in the soap mass; during this heating period, the temperature of the kettle contents will have risen to about 310-340°F. When the temperature is in the latter range, the formation of the complex soap from the normal barium soap and the excess barium hydroxide begins and proceeds vigorously. This reaction is exothermic and the temperature should be restricted to 375°F. or lower by the introduction of water into the kettle jacket or by the addition of oil to the soap mass, if necessary. When the free barium hydroxide content has reached a value of about 0.50 per cent, the remainder of the oil is added with constant stirring as rapidly as it can be accepted by the kettle contents. From this point on, the grease may be finished in a number of ways, one commonly used method being to cool the grease to a temperature below 210°F. and add a small quantity of water (0.2% to 3.0%). The grease is then partially dehydrated at an elevated temperature to develop the proper grease body, drawn into pans, cooled, and subsequently worked or homogenized to bring it to a smooth non-fibrous consistency.

Barium greases have been prepared from a wide variety of soap stocks, such as tallow, lard oil, cottonseed oil, horse fat and the like, combinations of these with one another or with fatty acids.

The barium hydroxide is readily available in commercial quantities as the hydrate, $Ba(OH)_2.8H_2O$. The amount of excess barium hydroxide used in compounding complex greases can be varied within a generous range, e.g. 40-60%, the particular range depending partly upon the kind of grease desired, upon the viscosity of the mineral oil present, etc.

Latitude in formulation is also possible in regard to the type and viscosity of the mineral oil used. A grease prepared with a naphthenic lubricating oil of 500 seconds Saybolt Universal at 100°F., for example, has given very satisfactory performance as a general-purpose lubricant. Valuable greases have also been prepared containing oils of higher and lower viscosity. Satisfactory greases have likewise been compounded from oils of widely varying types and in this respect, the formulating of barium greases is comparable with that of the more common greases containing calcium or sodium soaps.

The water content may be varied considerably, since it is not critical as in the case of many other greases. It is desired only to keep the water content low enough to insure suitably high melting points, acceptable appearance and good performance for prolonged periods at elevated temperatures.

Finally, as to variations in the actual compounding procedure used, in most respects that is ample leeway as to operations without the quality of the product being affected. Consequently, the correction of any irregularity in a batch operation presents no more serious problem than in the case of the more conventional greases.

The Properties of Complex Barium Soap Greases

The commercial barium soap greases of the complex type are unctuous, thoroughly milled greases of non-fibrous or buttery texture, which resemble in appearance the calcium soap greases of generally comparable composition. The following data are typical for one of the barium soap greases being extensively marketed at the present time on the Pacific Coast:

Barium soap, %	22.0
Free alkali, %	0.05
Free fat, %	0.3
Water, %	0.15
Unsaponifiable matter, including mineral oil and glycerin (by diff)	77.50
Total, %	100.00
ASTM penetration at 77°F. (unworked)	240-260
ASTM penetration at 77°F. (worked)	240-260
ASTM dropping point, °F.	350+

It will be noted that the soap content is appreciably higher than that of the sodium and calcium soap greases and considerably higher than that of the lithium and aluminum soap greases of comparable ASTM penetration. Although it is recognized that the question of soap content versus lubricating efficiency is a controversial subject in the grease industry, it is believed that the long record of eminently satisfactory lubrication performance, frequently under adverse conditions where no other grease was adequate, is sufficient evidence that high soap content is not a detriment insofar as barium greases are concerned. Further, it is felt that a comparison between different types of greases solely upon the basis of soap content is rather a pointless argument unless proper cognizance is taken of the differences in the molecular weights of the bases, of the ultimate effectiveness of the greases in lubricating bearing surfaces under service conditions, and of the various factors of

composition that radically modify the oil-thickening action of the different soaps.

The free alkalinity or free acidity of the grease is maintained as near neutrality as practical, a free alkali content of approximately 0.05% being considered typical. However, as is so often observed, a slight amount of free acidity imparts added stability to the grease without evident objectionable effects.

A glycerin content seems to be desirable, and it has been found preferable to employ a quantity of the straight glycerides as a portion of the soap stock along with a moderate percentage of fatty acids. A water content also seems to be desirable, such as 0.1 per cent. However, it has been found that, depending upon the soap stocks employed, good greases may possess water contents of 0.4 per cent.

The ASTM penetration of the commercial barium grease is not subject to marked change upon further working, either in the ASTM grease worker or in high speed bearings, because it is already severely milled before being packaged. In this respect, it is very similar to the familiar sodium soap ball-bearing greases distributed in the trade. Moreover, these two types of greases also undergo approximately the same degree of breakdown in penetration during the same severe milling operation, a fact which is of interest from the viewpoint of high temperature lubrication. Milled barium greases frequently exhibit an anomalous effect in that they actually harden appreciably upon being worked in the ASTM grease worker, instead of showing the customary breakdown. Because the milled barium soap grease, like the usual milled sodium soap greases, does not exhibit excessive breakdown in grease structure upon being further severely worked, it is particularly effective in lubricating bearings involving excessive mechanical agitation, for example, wheel bearings.

The ASTM dropping point of the barium soap grease, it will be noted, exceeds 350°F. However, normally these greases have not been recommended for continued use when temperatures are in excess of about 250°F. This is due to the fact that maintaining the present barium greases at temperatures of about 300°F. or higher for prolonged periods causes a gradual change in structure leading to eventual degradation of the grease body. On the other hand, if the normal bearing temperature is below 250°F. but due to some cause or other peaks of 300°F. or higher are encountered for relatively short periods of time, satisfactory lubrication is obtained and there is no tendency for the grease to melt and run out of the bearing. In special cases it has been possible to give continued effective lubrication at temperatures in excess of 250°F.

The high water resistance of the subject barium soap greases is particularly important, because this property and the high heat resistance represent two of the principal reasons why these greases can be employed advantageously as all-purpose lubricants. No standard test is available for evaluating greases in respect to their water resistance, but of the various laboratory tests currently employed for the purpose, it is thought that the Navy water absorption and leaching tests (Specification 14L5) are probably to be preferred for indicating in a preliminary way and with a fair degree of assurance, approximately what can be expected from the respective greases in actual service, particularly when vigorous mechanical agitation is a factor. By these tests, the barium, calcium and lithium soap greases are comparable in respect to their water resistance. If other tests, such as boiling water tests and the like, are employed, essentially the same general grouping of the various type greases will result. The water resistance of the greases will be affected considerably by the hardness and the composition of the grease, depending for instance upon the amount of soap present, the presence of glycerin, the viscosity of the oil, etc. All of the barium soap greases prepared to date have shown acceptable water resistance when tested by the commonly used procedures for evaluating greases in respect to this particular property. Service performance has strikingly confirmed the results of such tests.

The heat resistance of the commercial barium soap greases is another property of major interest. From the method of manufacture and from the fact that the barium soap greases do not undergo a radical change in physical structure when heated to high temperatures (above 225°F.) and then recooled, it will be evident that this type of grease should manifest a very favorable heat resistance under service conditions and, in fact, barium and sodium soap greases behave similarly in this respect. Other commonly used greases, when heated to elevated temperatures and recooled, either become unstable because of loss of water or show a marked and undesirable change in physical structure. Further, the physical structure of still other types of greases, although moderately satisfactory for lubricating high speed bearings at ordinary temperatures, breaks down as a consequence of mechanical working at elevated temperatures.

The relative temperature susceptibility of greases is frequently represented by penetration data at various temperatures. This method of comparison, as in the case of the ASTM dropping point, can lead to serious misunderstandings unless allowance is made for the changes in the physical structures of the greases at elevated temperatures. For

example, merely to cite the penetration data for heavily gelling aluminum greases at 140-200°F. would be misleading unless it were also understood that such greases possessed a viscous gel structure making such a product, unless modified, unsatisfactory for lubrication at these temperatures. In the case of sodium, calcium, and barium soap greases, however, data of this kind can be presented so that one may gain a reasonably accurate impression of how such greases change in penetration and appearance with temperature. The following data indicate how the above three types of greases compare in respect to their temperature-consistency coefficients over a wide range of temperature:

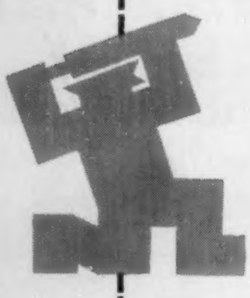
TABLE 1

Abraham Consistency[2] (worked grease)

Type of Grease	0°F.	40°F.	77°F.	100°F.	140°F.	180°F.	240°F.	300°F.
Calcium—(Pale)	3.1	2.9	2.8	2.6	2.5	....	....	....
Calcium—(Black)	3.9	3.1	2.9	2.8	2.6	2.1	....	....
Barium	3.7	3.4	3.2	3.0	2.6	2.5	2.2	....
Sodium (Short fibre)	3.3	3.1	2.8	2.7	2.4	2.3	2.4(a)	2.2

(a) This hardening effect has also been observed with other samples of sodium greases.

All four greases represent regularly marketed products prepared with a soap stock, of which at least 85% is prime tallow, or a mixture of prime tallow and tallow fatty acids. With the exception of the grease shown as calcium (pale), the greases were prepared with oils varying from 55 to 70 seconds Saybolt Universal at 210°F. The calcium (pale) grease was prepared with an oil possessing a Saybolt Universal viscosity of 42 seconds at 210°F. Abraham consistency data are presented here rather than ASTM penetration data, merely because the original tests were more conveniently made using this test, and direct conversion of the data to ASTM penetration cannot accurately be made. For those not conversant with this test, it is pointed out that progressively higher values represent a hardening of the grease.



The comparative behavior of the greases as indicated by the above data can be qualitatively confirmed by merely heating or cooling samples of the four greases simultaneously and stirring the samples with a thermometer to note the temperatures and relative hardnesses of the greases. It is clear from these data that the three types of greases thin out at approximately the same rate over a wide temperature range, and it is of particular interest to note that between 0°F. and 240° F., the consistencies of both the barium and sodium soap greases change in a generally comparable manner. An interesting comparison of the above greases could probably also be drawn from pressure viscosity data obtained through the use of a pressure viscosimeter similar to the apparatus[3] described at a previous convention (1942).

A discussion of the heat resistance of barium greases properly includes comments relative to its oxidation resistance. The Norma-Hoffman oxidation bomb test is the most widely used method of determining the oxidation resistance of greases, and although it may be difficult to correlate the test data with full service performance, it is believed that the test differentiates relatively good greases from inferior products. Using this bomb test at 210°F., with glass trays, without catalyst, and with 110 lb. per square inch of oxygen, complex barium soap greases showed an induction period of 96 hours. This result compares favorably with those for other uninhibited greases prepared from similar quality soap stocks and mineral oil. Moreover, the residue from the test was similar to that remaining from sodium soap greases after the same test; it was slightly harder and darker than the original grease but otherwise unchanged. This oxidation test is a severe one, and other type greases without inhibitors will frequently show serious syneresis, liquefaction, or an objectionable change in grease structure. The use of oxidation inhibitors in barium greases will extend the induction period as in the case of other greases.

(To Be Continued)

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